# Stokes and Antistokes Raman Scattering in Heteronuclear and Homonuclear Molecules

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**ABSTRACT:** Raman scattering is a consequence of quantized vibrations or rotations of molecules irradiated with monochromatic light. Some light is scattered at the same frequency (Rayleigh) and some light is scattered at different frequencies (Raman). The difference in frequency corresponds to the energy of vibrational transition. The Raman scattering can be divided into two parts, the Stokes line and the anti-stokes line. For the Stokes line the energy of the scattered radiation is less than the incident radiation, so there is a loss of energy and a longer wavelength results. For the anti-stokes line the energy of the scattered radiation is more than the incident radiation, so there is a gain of energy and a shorter wavelength results. There are two types of Raman spectroscopy: rotational Raman and vibrational Raman spectroscopy. A detailed study of the wave-numbers and wavelengths of the rotational and vibrational Raman lines (Stokes and anti-Stokes) are given in this article.

**KEYWORDS:** Raman Scattering, Rayleigh scattering, Stokes Raman Lines, Anti-stokes Raman Lines, Rotational Raman Spectra, Vibrational Raman Spectra, S-Branch, O-Branch.

## 1. INTRODUCTION

Raman spectroscopy measures the scattering of light by matter [1]. The light source used in Raman spectroscopy is a laser [2]. The laser light is used because it is a very intense beam of nearly monochromatic light that can interact with molecules of a gas or liquid or transparent solid sample [3, 4]. When matter absorbs light, the internal energy of the matter is changed in some way. When the radiation is absorbed, a molecule jumps to a higher vibrational or rotational energy level. When the molecule relaxes back to a lower energy level, radiation is emitted. Most often the emitted radiation is of the same frequency as the incident light. Since the radiation was absorbed and then emitted, it will likely travel in a different direction from which it came. This is called Rayleigh scattering [5, 6]. The intensity of the scattered light is inversely proportional to the fourth power of wavelength. Sometimes, however, the scattered (emitted) light is of a slightly different frequency than the incident light, *i.e.* scattering light also contains some weak additional lines having slightly different frequencies than the Rayleigh scattering line. This effect was first noted by C.V Raman who won the Nobel Prize for this discovery [5-7]. The effect, named for its discoverer, is called the Raman effect, or Raman scattering. A comparison of the wave numbers of these additional lines shows that

these Raman lines are independent of the wavelength of the incident light but depends on the nature of scattering substance. For different scattering samples, the displacements of the Raman lines from the incident laser light are different. Thus, the displacements are characteristics of the scattering sample. Raman scattering occurs in two ways. If the emitted radiation is of lower frequency than the incident radiation, then it is called Stokes scattering. If it is of higher frequency, then it is called anti-Stokes scattering.

Raman spectroscopy is often considered to be complementary to IR spectroscopy [1]. For symmetrical molecules with a center of inversion, Raman and IR are mutually exclusive. In other words, bonds that are IR-active will not be Raman-active and vice versa. Other molecules may have bonds that are either Raman-active, IR-active, neither or both.

In this article, we will discuss about the classical and quantum theory of Raman spectra of heteronuclear and homonuclear diatomic molecules. The theoretical explanation of Stokes Raman scattering lines and Anti-stokes Raman scattering lines corresponding to pure rotational and vibrational Raman spectrum are also

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discussed.

## 2. Theoretical Explanation of Raman Effect

When considering Raman scattering, we can think about the physics in one of two ways: the classical wave interpretation or the quantum mechanical interpretation.

### 2.1 Classical Theory of Raman Effect

When an atom or molecule is brought into an electric field $\vec{E}$, an electric dipole moment $\vec{\mu}$ is induced in the system [4]. The magnitude of this induced dipole moment is proportional to the electric field,

$$\vec{\mu} = \alpha\vec{E} \qquad ...(1)$$

where $\alpha$ is known as the polarizability.

Except for the case of spherical symmetry, the magnitude of the induced dipole moment depends on the direction of the electric field [3].

For example, in case of a diatomic molecule, the induce dipole moment will be higher in magnitude when the electric field direction is along the inter-nuclear axis than that of the perpendicular to the inter-nuclear axis [4].

If a light of frequency $\nu_{ex}$ is incident, then $\vec{E} = \vec{E}_0 \sin(2\pi\nu_{ex}t)$, then the dipole moment will be from equation (1),

$$|\vec{\mu}| = \alpha|\vec{E}_0| \sin(2\pi\nu_{ex}t) \qquad ...(2)$$

So, the dipole will also oscillate with frequency $\nu_{ex}$. According to classical electromagnetic theory, when a dipole oscillates, it radiates with the same frequency of oscillation. This is nothing but the Rayleigh scattering as discussed before.

Now, if the molecule vibrates i.e., the internuclear distance changes. And also this polarizability depends on the orientation of the molecule. So, the rotation of the molecule also changes the polarizability.

Now, we can write the polarizability for vibration

$$\alpha = \alpha_{0v} + \beta_v \sin(2\pi\nu_{vib.}t)$$

where $\alpha_{0v}$ the polarizability in the equilibrium position, $\nu_{vib.}$ is the vibrational frequency and $\beta_v$ is the proportionality constant $\beta_v \ll \alpha_{0v}$.

Similarly, for rotation we can write,

$$\alpha = \alpha_{0r} + \beta_r \sin(2\pi 2\nu_{rot.}t)$$

Here the frequency with which the polarizability changes during rotation is twice the rotational frequency (see figure). The reason for this is that, the polarizability is same for that of the opposite field.
Now,

$$\vec{\mu} = \alpha\vec{E}$$

$$\vec{\mu} = [\alpha_{0v} + \beta_v \sin(2\pi\nu_{vib.}t)]\vec{E}_0 \sin(2\pi\nu_{ex}t)$$

$$\vec{\mu} = [\alpha_{0v}\vec{E}_0 \sin(2\pi\nu_{ex}t) + \beta_v\vec{E}_0 \sin(2\pi\nu_{vib.}t)\sin(2\pi\nu_{ex}t)]$$

$$\vec{\mu} = \Bigg[\alpha_{0v}\vec{E}_0 \sin(2\pi\nu_{ex}t) + \frac{1}{2}\beta_v\vec{E}_0[\cos 2\pi(\nu_{ex}-\nu_{vib.})t - \cos 2\pi(\nu_{ex}+\nu_{vib.})t]\Bigg] \quad ...(3)$$

Similarly, for rotation

$$\vec{\mu} = \Bigg[\alpha_{0r}\vec{E}_0 \sin(2\pi\nu_{ex}t) + \frac{1}{2}\beta_r\vec{E}_0[\cos 2\pi(\nu_{ex}-2\nu_{rot.})t - \cos 2\pi(\nu_{ex}+2\nu_{rot.})t]\Bigg] \quad (4)$$

Thus, we see from equation (3) that the induced dipole moment not only oscillates with frequency $\nu_0$ but also with other displaced frequency $(\nu_{ex}+\nu_{vib.})$ and $(\nu_{ex}-\nu_{vib.})$ in case of vibration.

For rotation, the displaced frequencies are $(\nu_{ex}+2\nu_{rot.})$ and $(\nu_{ex}-2\nu_{rot.})$. So, the scattered light contains displaced lines on both the sides of undisplaced line and the separations in both cases are same. Frequency on lower side is known as Stokes lines and on higher side is known as anti-stocks lines as shown in Fig. 1.

The experimental Raman spectrum shows that the intensities of the Stokes lines are higher than that of the anti-Stokes lines. The classical explanation does not provide information about intensity for both the lines and thus inadequate for explaining the experimental spectrum.

### 2.2 Quantum Theory of Raman Effect

Let us consider for a system, $E_0$ is the ground electronic state and $v = 0, 1, ......$ are the vibrational states of the ground electronic state. If the light frequency $\nu_{ex}$ incident on this system, three cases may arise:
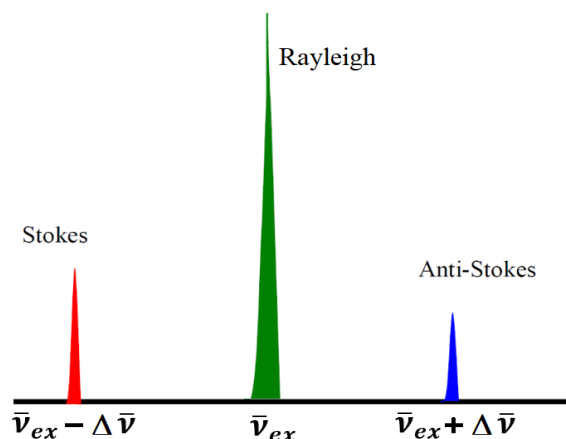
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**Fig. 1 Intensity and wave-numbers of Stokes and Anti-stokes scattered lines with respect to Rayleigh scattered line.**
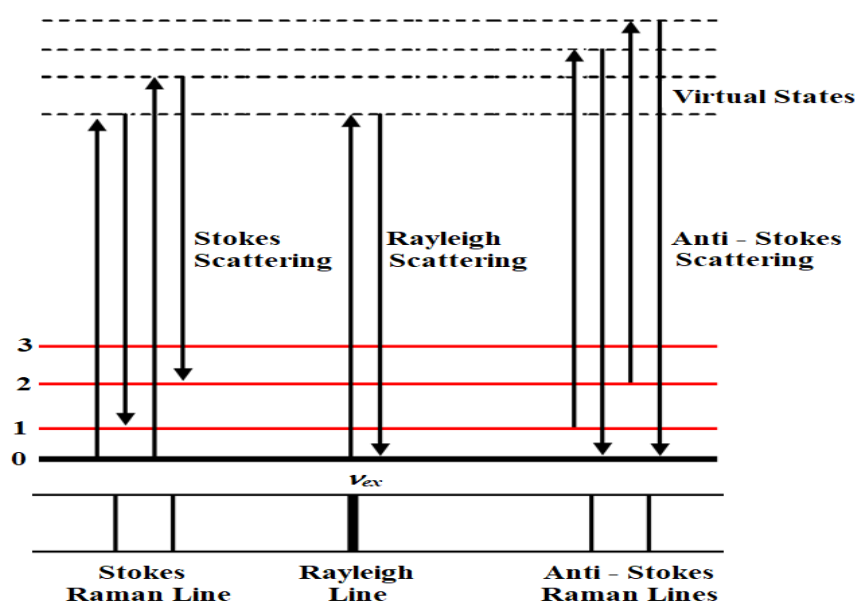


**Fig. 2 Energy level diagram showing the Rayleigh scattering line, Stokes Raman scattering line, and anti-Stokes Raman scattering line.**

**Case–I:** Molecules absorb the light of frequency $h\nu_{ex}$ and go to the vibrational state as shown by dashed line in the Fig. 2. The vibrational state is created by the light and molecular interaction and exists as long as the light exists [10]. It is not the eigen state of the system but is a linear combination of all the eigen states of the molecule. Thus, by definition, the lifetime of the virtual state is very small. Now the molecules will back to the ground vibrational state ($v = 0$) and will emit the same frequency $\nu_{ex}$. This is the same Rayleigh scattering [10].

**Case–II:** Molecules are transferred to the vibrational state by light $\nu_0$ and these excited molecules may come back to the higher

vibrational state ($v = 1$). In this case the emitted frequency is ($\nu_{ex} - \nu_{vib.}$). According to the energy conservation, the energy will be lost from the incident photon energy $h\nu_0$ to excite the vibrational frequency of the molecule and thus, the emitted photon energy

$$h\nu_{stokes} = h\nu_{ex} - h\nu_{vib.} = h(\nu_{ex} - \nu_{vib.})$$

**Case–III.** In thermal equilibrium, the excited vibrational levels are also populated and molecules there can also absorb light and go to the virtual state. While coming back to the same vibrational state, this will emit frequency $\nu_0$. But if molecules come back to ground vibrational state ($v = 0$) then the emitted frequency will be

$(v_{ex} + v_{vib.})$. Again, according to the energy conservation, the photon energy adds up the vibrational energy and emitted energy will be

$$h\nu_{anti-stokes} = h\nu_{ex} + h\nu_{vib.} = h(\nu_{ex} + \nu_{vib.})$$

Since, the number of molecules in the excited state is very small, the chances of this collision are very small. Hence Anti-stokes Raman line is much weaker than Stokes Raman line.

## 3. Pure Rotational Raman Spectra of Diatomic Molecules

The rotational energy levels of linear molecules is

$$\varepsilon_J = BJ(J + 1) - DJ^2(J + 1)^2 \, cm^{-1}$$

where $J = 0, 1, 2, 3, ..........$

But in Raman spectroscopy, the precision of the measurements does not normally warrant the retention of the term involving $D$, the centrifugal distortion constant [8].
So, we take

$$\varepsilon_J = BJ(J + 1) \, cm^{-1}$$

where $J = 0, 1, 2, 3, ..........$

The selection rule for the pure rotational Raman spectra of diatomic molecules is:
$\Delta J = 0, \pm 2$ only.

The selection rule $\Delta J = 0$ gives rise to the Rayleigh scattering only.

The selection rule $\Delta J = \pm 2$ gives rise to the Raman lines. The factor 2 is due to the fact that the polarizability ellipsoid rotates twice as fast as the rotation of the molecule.
For transition $J' \rightarrow J''$, the wave number is given by

$$\bar{v}_{J' \rightarrow J''} = \Delta \varepsilon_J = \varepsilon_{J''} - \varepsilon_{J'}$$

$$\bar{v}_{J' \rightarrow J''} = BJ''(J'' + 1) - BJ'(J' + 1)$$

$$\bar{v}_{J' \rightarrow J''} = B(J''^2 + J'') - B(J'^2 + J')$$

$$\bar{v}_{J' \rightarrow J''} = B[(J''^2 - J'^2) + (J'' - J')]$$

$$\bar{v}_{J' \rightarrow J''} = B(J'' - J')(J'' + J' + 1)$$

For $\Delta J = +2 \Rightarrow J' + 2 = J''$ or $J'' - J' = 2$

$$\bar{v}_{J' \rightarrow J'', \ J' < J''} = B(2)[(J' + 2) + J' + 1]$$

$$\bar{v}_{J' \rightarrow J'', \ J' < J''} = +B(2)(2J' + 3)$$

$$\bar{v}_{J' \rightarrow J'', \ J' < J''} = +B(4J' + 6)$$

Where $J' = 0, 1, 2, 3, ..........$

For $\Delta J = -2 \Rightarrow J' = J'' + 2$ or $J'' - J' = -2$

$$\bar{v}_{J' \rightarrow J'', \ J' > J''} = B(-2)[J'' + (J'' + 2) + 1]$$

$$\bar{v}_{J' \rightarrow J'', \ J' > J''} = -B(2)(2J'' + 3)$$

$$\bar{v}_{J' \rightarrow J'', \ J' > J''} = -B(4J'' + 6)$$

Where $J'' = 0, 1, 2, 3, ..........$

Thus, Raman lines will appear at wave number given by expression

$$\bar{v} = \bar{v}_{ex} \pm B(4J + 6)$$

Here, the plus sign refers to anti-stokes lines and minus to stokes line and $\bar{v}_{ex}$ is the wavenumber of the exciting radiation (*i.e.* Rayleigh line).
The expected pure rotational Raman spectrum is shown in Fig. 3.
The first stokes and anti-stokes line will lie at a separation of $6B$ from the Rayleigh line. The remaining lines will lie at a constant spacing of $4B$.

## 4. Pure Vibrational Raman Spectra

For every vibrational mode we can write an expression of the form:

$$\varepsilon_v = \bar{\omega}_e \left( v + \frac{1}{2} \right) - \bar{\omega}_e x_e \left( v + \frac{1}{2} \right)^2$$

where, $v = 0, 1, 2, 3, ...................$

where, $\bar{\omega}_e$ is the equilibrium vibrational frequency and $x_e$ is the anharmonicity constant [9]. Such an expression is perfectly general, whatever the shape of the molecule or the nature of the vibration.

The selection rules for the vibrational Raman spectra are the same as those for pure vibrational spectra *i.e.* $\Delta v = \pm 1, \pm 2, ......$ The probability of $\Delta v = \pm 2, \pm 3, ........$decreasing rapidly.
Particularizing, now to Raman active modes, we can apply selection rule to the energy level expression given above, so
$\Delta \varepsilon_{fundamental} = \bar{\omega}_e (1 - 2x_e) \, cm^{-1}$
$\Delta \varepsilon_{first \ overtone} = 2\bar{\omega}_e (1 - 3x_e) \, cm^{-1}$
$\Delta \varepsilon_{second \ overtone} = 3\bar{\omega}_e (1 - 4x_e) \, cm^{-1}$
$\Delta \varepsilon_{hot \ band} = \bar{\omega}_e (1 - 4x_e) \, cm^{-1}$

Since the Raman scattered light is, in any case, of low intensity we can ignore completely all the weaker effects such as overtones and 'hot bands', and restrict our discussion merely to the fundamentals [7].
We would expect Raman lines to appear at distances from the exciting line corresponding to each active fundamental vibration. So, we can write

$$\bar{v}_{fundamental} = \bar{v}_{ex} \pm \Delta \varepsilon_{fundamental} \ cm^{-1}$$

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$$\bar{v}_{fundamental} = \bar{v}_{ex} \pm \bar{\omega}_e(1 - 2x_e) \ cm^{-1}$$

where the minus sign represents the Stoke's lines (*i.e.* for which the molecule has gained energy at the expense of the radiation) and the plus sign refers to the anti-Stoke's lines. The latter are often too weak to be observed, since as we saw earlier, very few of the molecules exist in the $v = 1$ state at normal temperatures.

The vibrational Raman spectrum of a molecule is, then, basically simple. It will show a series of reasonably intense lines to the low-frequency side of the exciting line with a much weaker, mirror image series on the high-frequency side. The separation of each line from the center of the exciting line gives immediately the Raman active fundamental vibration frequencies of the molecule [7].

The vibrational Raman spectra of homonuclear diatomic molecules are of special interest because they yield force constant and rotational constant that are not available from infrared absorption spectroscopy.
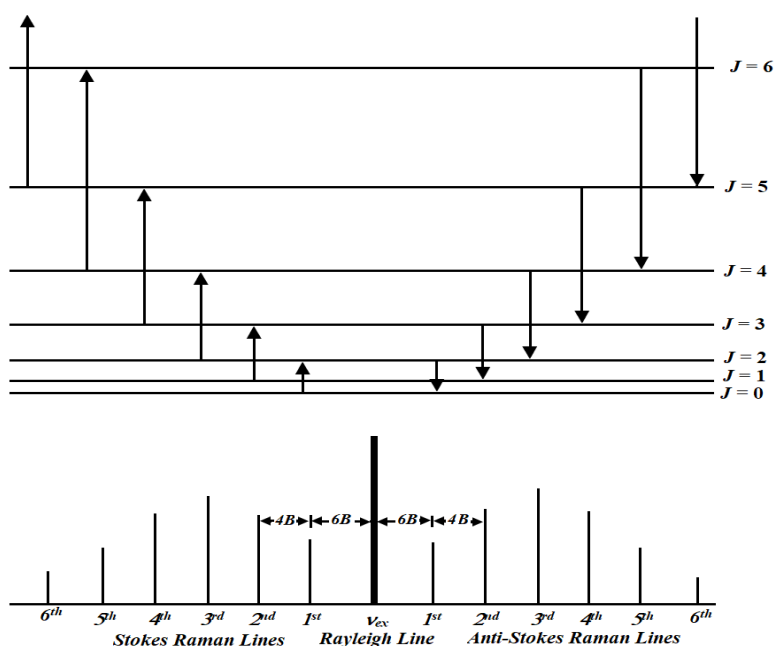


**Fig. 3. Rotational transitions and Stokes and Anti-stokes Raman lines in Rotational Raman spectrum**

## 5. Relation between Wave-Numbers of Rayleigh Line, Stokes Raman Line and Anti-Stokes Raman Line

The wave-number of Stokes line is given by
$$\bar{v}_S = \bar{v}_{ex} - \Delta\bar{v} \qquad ...(5)$$
The wave-number of Anti-Stokes line is given by
$$\bar{v}_A = \bar{v}_{ex} + \Delta\bar{v} \qquad ...(6)$$
Adding equation (5) and (6), we get
$$\bar{v}_S + \bar{v}_A = 2\bar{v}_{ex}$$
$$\bar{v}_{ex} = \frac{\bar{v}_S + \bar{v}_A}{2}$$
Thus, the wave-number of Rayleigh line (incident radiation) is equal to the arithmetic mean of wave-numbers of Stokes and Anti-Stokes Raman lines.

## 6. Relation between Wavelengths of Rayleigh Line, Stokes Line and Anti-Stokes Line
The wave-number of Stokes line is given by
$$\bar{v}_S = \bar{v}_{ex} - \Delta\bar{v}$$

$$\Delta\bar{v} = \bar{v}_{ex} - \bar{v}_S \qquad ...(7)$$

The wave-number of Anti-Stokes line is given by
$$\bar{v}_A = \bar{v}_{ex} + \Delta\bar{v}$$

$$\Delta\bar{v} = \bar{v}_A - \bar{v}_{ex} \qquad ...(8)$$

Adding equations (7) and (8), we get
$$\bar{v}_{ex} - \bar{v}_S = \bar{v}_A - \bar{v}_{ex}$$

$$\frac{1}{\lambda_{ex}} - \frac{1}{\lambda_S} = \frac{1}{\lambda_A} - \frac{1}{\lambda_{ex}}$$

$$\frac{2}{\lambda_{ex}} = \frac{1}{\lambda_A} + \frac{1}{\lambda_S}$$

$$\lambda_{ex} = \frac{2\lambda_S\lambda_A}{\lambda_S + \lambda_A}$$

Thus, the wavelength of Rayleigh line (incident radiation) is equal to the harmonic mean of

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wavelengths of Stokes and Anti-Stokes Raman lines.

## 7. CONCLUSION

This article explains the classical and quantum theory of Raman spectra of heteronuclear and homonuclear diatomic molecules. The theoretical explanation of Stokes Raman scattering lines and Anti-stokes Raman scattering lines corresponding to pure rotational and vibrational Raman spectrum are discussed in detail. The wave-number of Rayleigh line (incident radiation) is equal to the arithmetic mean of wave-numbers of Stokes and Anti-Stokes Raman lines. The wavelength of Rayleigh line (incident radiation) is equal to the harmonic mean of wavelengths of Stokes and Anti-Stokes Raman lines.

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